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DEVELOPMENT OF A MICROPATTERNED ELECTRODE FOR STUDIES OF ZINC ELECTRODEPOSITION

D.P. Sutiya*, R.H. Muller, and C.W. Tobias
(*M.S. Thesis)

December 1986

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FOR STUDIES OF ZINC ELECTRODEPOSITION

Davor P. Sutija
(M.S. Thesis)

with

Rolf H. Muller and Charles W. Tobias
Department of Chemical Engineering
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

Procedures have been developed for the preparation of a micropatterned electrode to be used in the study of electrocrystallization. Using microphotolithography, in conjunction with evaporation and pulse electrodeposition of thin films, a set of artificially roughened electrodes with hemispherical surface features five microns in diameter was developed. By controlling the orientation and separation of such protrusions, the experimenter may study the interaction of growth centers and the genesis of striations.

Voltammetric studies were conducted to determine the material best suited for use as a permanent electrode surface in the fabrication of the micropatterned substrate and in stripping coulometry. Gold, platinum, and various carbon surfaces were evaluated for zinc nucleation density and hydrogen overpotential. Surface homogeneity was examined by

both light and scanning electron microscopy. Gold was determined to possess the best combination of material properties: chemical inertness, low melting point, and a high work function allowing underpotential deposition of zinc which reduces the rate of hydrogen evolution:

Stripping coulometry was employed to determine zinc limiting currents, and evaluate effective diffusion coefficients in concentrated zinc chloride solutions. Although the method worked well for dilute zinc chloride and copper sulfate solutions, it failed at higher current densities; the emergence of surface roughness obscured actual limiting current plateaus.

I. INTRODUCTION

1.1 Zinc Battery Research

Rechargeable batteries are under consideration for energy storage applications. Such applications include utility load-levelling, use in remote locations in conjunction with photovoltaic arrays, and as power supplies for electric vehicles [1, 2]. Among the various battery systems under study, acidic zinc-halide batteries are attractive because of their low material cost, fast kinetics, large cell voltages, and moderate specific energy. Furthermore, these systems are operated at room temperature; a natural advantage over sodium-sulfur and lithium/FeS₂ systems.

Both the ZnCl₂ and the ZnBr₂ batteries involve a flow system, but the chloride battery design is simpler since the chlorine is stored as a hydrate in a separate chilled compartment and no internal separator is required. The bromide battery design differs in that the bromine is complexed with a quaternary-ammonium compound. Therefore, the ZnBr₂ battery requires a separator to prevent the bromine from attacking and hence corroding the zinc. Figure 1.1 shows schematic diagrams of the two acid-halide cells.

The main limitations to successful development are low current efficiency (roughly 60–70%) and limited demonstrated cycle life (100 – 300 cycles) [1]. One reason for the short lifetime of the cell is the uneven zinc deposit upon successive recharging. Striated deposits, consisting of more or less evenly spaced ridges aligned in the direction of flow, develop at current densities well below the limiting value. Such contoured deposits lead to material loss upon discharge since certain

regions dissolve preferentially, and non-adhering portions of the deposit accumulate at the base of the cell. Catastrophic failure may occur as a conductive bridge is formed at the bottom of the cell, or as ohmically favored dendrites short across the cell gap during charging. Such dendrites are very often formed at the ridges of striations. Understanding the emergence of uneven deposits and the initiation of striations may lead to a better design for these promising battery systems.

1.2 Scope of Present Work

The long term goal of this research project is to understand, both theoretically and phenomenologically, the emergence of striated deposits during zinc deposition at low current densities. Such deposits are characterized by ridges and valleys aligned in the direction of flow.

Until recently, work on the morphology of electrodeposited zinc was generally qualitative in nature, and observations were on a macroscopic scale. McVay's introduction of video microscopy, an in situ method which permits more detailed observation of the genesis of striations, made it possible to focus on the effect of single protrusions [21].

The cause of striations seems to be enhanced deposition behind growth centers which develop from randomly occurring nucleation sites. Micro-turbulence and Taylor-Goertler vortices may play a role in such an enhancement mechanism [3]. To investigate these ideas, two parallel areas of research were pursued. First, the development of a micro-patterned electrode to study the effect of electrode morphology on striation emergence, and secondly, the use of stripping coulometry to

calculate effective diffusion coefficients in concentrated zinc chloride solutions by measuring limiting current plateaus.

As a first step, the suitability of various electrode surfaces was examined. Cyclic Voltammetry was used to study the activity of gold, platinum and graphite electrodes, in order to better understand the various reactions occurring simultaneously during both electrode preparation procedures and subsequent zinc deposition.

A number of different carbon and graphite surfaces were tested: Gould Synthetic graphite, glassy or vitreous carbon, Exxon graphite-loaded polymer, and pyrolytic graphite of various types, most notably Union Carbide highly-oriented pyrolytic graphite (HOPG). Carbon electrodes showed promise since they tended to exhibit high hydrogen overpotentials and a broad 1.5 Volt range over which they were essentially ideally polarizable with background currents of less than one microamp, and a capacitance of 40-100 microfarads.

Gold and platinum surfaces, however, were selected for the micro-patterned electrode, because metals are more easily polished and adhere well to thin films of evaporated and electrodeposited metal. The micro-patterned electrode developed has protrusions five microns in diameter on an otherwise optically smooth surface. These protrusions mimic the effect of growth centers, but allow the investigator to control the placement of such centers and thereby study their interaction. Figure 1.2 shows one such electrode, with half of the surface arranged in a square pitch, and the other half in a triangular pattern. The surface features on the gold and platinum electrodes are made by advanced VLSI techniques. After implanting such an electrode in an epoxy base and

placing it in a flow cell designed for in situ optical observation and video recording, the phenomena of growth center coalescence and striation formation may be studied.

To predict the effect of protrusions on recirculation, an accurate value of the diffusion boundary layer thickness must be determined, since the effects of protrusions scale with this length. Diffusion coefficients for ZnCl_2 available in the literature are inadequate for a number of distinct reasons. Because of the occurrence of polarographic maxima, associated with the effects of zinc nucleating on the liquid mercury surface, polarographically determined diffusion coefficients become unreliable precisely at the high concentrations which are of greatest interest [44,45]. Binary diffusion coefficients, in the absence of potassium chloride, obtainable from the interferometric work of Rard and Miller, are also unsatisfactory since they do not take into account the complexing of zinc with excess chloride ions [43]. These complexes tend to decrease the transference number of zinc in solution and thereby lower the effective diffusion coefficient.

A common method of determining limiting current densities involves the use of a rotating disk electrode. By sweeping the potential (or current) cathodically, in the absence of competing faradaic processes, one obtains a plateau at the diffusion limit corrected for migration. From this data, one may calculate the diffusion coefficient by use of the Levich equation. This method was used by Faltemier, Rajhenbah, and Tobias, but due to concomitant hydrogen evolution, their calculated diffusivity varied with rotation speed and scan rate, and plateaus could

only be observed at very low concentrations (i.e. less than 0.1 M ZnCl_2) [38].

To obtain an accurate value for the proper zinc limiting current, corrected for hydrogen coevolution, a method first used by Rogers and Taylor in alkaline solutions, was employed [46]. Their method, known as stripping coulometry, is based on measuring the total current passed during galvanostatic deposition, then stepping the potential to a value anodic of zinc deposition and measuring the amount passed during potentiostatic dissolution. The hydrogen evolved cathodically is no longer present at the electrode and the charging current due to stepping the potential is negligible.

Understanding the role of growth centers in creating secondary flows, coupled with the proper diffusion layer thickness as a function of position on the zinc electrode may make it possible to completely predict the location, size, and number of emerging striations.

1.3 Zinc Deposit Morphology

Research efforts in this laboratory over more than two decades have addressed the questions concerning the interaction between deposit morphology and hydrodynamic flow [24, 75]. The study of zinc deposition began in 1976 with the initial work of Milan Jaksic [12]. Jaksic, later with the collaboration of James Faltemier, Tetsuake Tsuda and Darko Rajhenbah, performed a series of studies in both chloride and sulfate solutions, over broad ranges of composition, current density, and flow rates [3, 14]. They observed the emergence of striated deposits, after an induction period, at conditions well below limiting current. Figure

1.3 shows typical striations obtained in a channel flow cell, and on a rotating disk [3].

The emergence of striated deposits is not in and of itself very startling. Rather, it is their occurrence at very low current densities (less than 10% of limiting current), and disappearance at higher current densities that is puzzling. Several authors have previously observed striations occurring in metal deposition and corrosion on rotating disk electrodes [5, 6], and Levich [4] uses the striated surface of a corroding metal to demonstrate the distribution of streamlines near the surface of a rotating disk.

Johnson and Turner [5] obtained spirals under galvanostatic deposition from an acidified 1M CuSO_4 solution containing the levelling agent thiourea. It may be interesting to note that the striations occurred at a point in the current-voltage curve where a very small increase in potential led to a substantial change in current density. Such a marked sensitivity to overpotential may be a necessary condition for the emergence of striations. Such sensitivity is characteristic of reactions with high exchange current densities. Zinc deposition from its halides is moderately reversible, with an exchange current density on the order of 1 mA/cm^2 [16, 35]. Therefore, by this criterion, the deposit could be expected to show such behavior.

Rogers and Taylor [6] obtained spirals from a Watts nickel plating bath and first postulated that these spirals were caused by the traces of the wakes of hydrogen bubbles growing at surface protrusions. The protrusions were much smaller than the height of the hydrodynamic boundary layer, however, which implies that local turbulence may not have

occurred. Later, flow visualization work by Hanson [7] showed that protrusions which exceed the diffusion boundary layer thickness, even if they fall short of the hydrodynamic boundary layer, lead to an increase in mass transfer through local recirculation in the wake of the protrusion. Hence, the protrusions themselves, rather than hydrogen bubbles seem to be the cause of spiral markings and striations.

Hickman and Tobias [8] had previously studied the effect of Taylor vortices and secondary convection due to density instabilities across a mass transfer boundary layer. Streaked electrodeposits were obtained, and attributed to the flow effects that develop under the influence of buoyancy forces.

Hill and Rogers [9, 10] associated spirals occurring during copper electrodeposition with submicroscopic defects, and again noted that striations emerge when the slope of the current-voltage curve becomes very steep, namely, when a small overpotential gradient results in large differences in the resulting current.

Carlson and Tobias [11] studied the effect of protruding nodules on copper electrodeposition and found that at or near limiting current, a one millimeter protrusion leads to enhanced deposition in the wake of the surface defect. The resulting enhanced deposit is located directly behind the bump at limiting current but is more spread out at $i = 0.9 i_{lim}$ as shown in Figure 1.4.

Jaksic and Faltemier [3, 12, 13], encouraged by these results, used a number of flow visualization methods such as time lapse photography, motion pictures, and scanning electron microscopy to study zinc deposition. They found that striations occur even if the cathode is placed in

a side wall or facing downward in a channel flow cell, as well as in a rotating disk configuration. Hence, buoyancy forces could not account for the resulting deposit morphology, as in the work of Carlson and Hickman [8, 11].

Faltemier's research showed that striations appeared at current densities below 80 mA/cm^2 in chloride solutions, and below 15 mA/cm^2 in sulfate solutions. Since spirals appeared in both strongly-complexed ZnCl_2 and weakly-complexing ZnSO_4 , it is likely that complexation is not the major factor responsible for the formation of striations.

Smooth, random protrusions appeared first, then grew laterally in the direction of flow as illustrated in Figure 1.5. They then joined others downstream producing ridges. Substrate material, surface roughness, and varying pH (from 1 to 5) were only of secondary importance. An increase in zinc concentration affected the number density of striations, presumably due to a corresponding increase in the nucleation rate.

A surprising observation was that for the rotating disk studies the striations emerged at the outside edge of the disk and grew upstream toward the center. Such spirals emerged where the primary current density was highest, and led Jaksic to examine the deposits obtained from the channel flow-cell more closely [12]. He found that protrusions at the leading edge were also a predominant cause of striations. However, Faltemier's experiments in a large cell, with electrodes 30 cm in length, showed that striations emerge uniformly and spontaneously over the entire electrode, thereby discounting the edge effect as the sole cause [3]. Jaksic also studied the effect of Zonyl-FSB, a levelling

agent produced by Dupont. This surfactant was found to inhibit outward growth, resulting in the almost instantaneous appearance and high number density of striations. The density of striations also increased with current density. As the deposit thickened, the grooves melded together. Above a threshold current density no striations appeared, yielding a relatively smooth deposit.

Work on the effect of impurities was done by Tsuda [14], in a rotating disk cell to test the suggestion that hydrogen-producing impurities may catalyze the emergence of striations [14]. Tsuda prepared ZnCl_2 solutions of varying purity from ultra-pure to analytical grade, then used zinc cementation at elevated temperatures (90°C) and filtration to further clean the solutions. Metallic impurities were then added to test their effects on the formation of striated deposits.

Purification by cementation with zinc increased the spiral formation time, while the further addition of lead acetate reduced it to the level of the non-purified solutions. The number density and slope (angle) of the spirals were not a function of the contaminants. Tsuda showed that the angle of the spirals was constant, and that they were logarithmic, as expected from hydrodynamic theory [15], rather than Archimedean, as stated by Johnson and Turner [5]. Tsuda's calculations are shown in Figure 1.6. The addition of lead, which inhibits hydrogen evolution, caused greater coalescence of striations and smoother deposits, although still showing spiral structure. Tsuda concluded that hydrogen overpotential did not determine the nature of the deposit. Tsuda also observed spirals growing outward from the center, in addition to those initiated at the edge of the rotating disk. His work clearly

shows that increasing the current density results in an increased number density of nuclei eventually yielding a smooth deposit [14].

The discovery of disparate loci of initiation led to the work by Rolfe Anderson [16]. His research focused on the emergence of micron-sized growth centers prior to striation initiation. Using potential-step techniques, Anderson attempted to correlate the number of such growth centers to the applied overpotential. The results were inconclusive, since the relationship is very sensitive to the surface structure of the substrate (i.e., prior history of the electrode used).

Nevertheless, Anderson demonstrated that growth center emergence precedes striation formation, and that the coalescence and alignment of such protrusions dictate the location of the subsequently formed striations. The potential showed a transient peak under galvanostatic conditions, and the magnitude of the peak was inversely related to the number of available nucleation sites. Since the emergence of striations occurs at very low overpotentials and zinc deposition is moderately reversible, even small changes in voltage may cause greatly different nucleation number densities.

Also of interest is the work by Epelboin [17], and his successors, notably Bressan and Wiart [18-20]. In a series of papers, they obtained an S-shaped polarization curve for the zinc deposition reaction. They interpret this as indicating an autocatalytic reaction with a fast intermediate step which gives rise to multiple steady states. While such bifurcations have become a popular theme in recent fluid mechanics and kinetic literature, in this case the results are less conclusive.

The potential region over which the polarization curve doubles back on itself is only two to four millivolts wide, after subtracting out the ohmic component. Besides the acknowledged experimental error in their uncompensated resistance, roughly four percent, their research completely ignores changes in surface area that accompany the deposition process. At a given overpotential, the nominal current density will rise as nucleation takes place, since such nucleation drastically increases the real surface area and the number of possible reaction sites. Furthermore, Epelboin et al.'s S-shaped curves are only obtained at very high mass transfer rates (2400-4000 rpm on a rotating disk) which indicates the occurrence of instantaneous nucleation followed by hemispherical growth during the initial stages of deposition. As Anderson's work shows, zinc deposition is confined to nodules during this early period of deposition. It is probable that increased surface area, rather than an autocatalytic step, accounts for the very slight backward tilt on selected polarization curves at high mass transfer rates.

The most recent work in the continuing elucidation of the causes of non-uniform zinc deposition conducted in our laboratory has been that of Laura McVay. Her work introduced the use of video recording as an in-situ method for the observation of the growth dynamics of zinc. McVay confirmed that protrusions generally elongate in the downstream direction, and form striations by coalescing with other growth centers. The rate of nucleation on foreign substrates was shown to determine whether striations are observed. Figure 1.7 shows the resulting deposit on platinum, which has a high nucleation number density, and on Gould syn-

thetic graphite at the same amount of charge passed. Both deposits show the imprint of hydrogen evolution, but only the one on graphite, with a lower nucleation density, developed striations. Although hydrogen evolution was observed at low pH, McVay's work discounts a key role for hydrogen in the formation of striations. McVay's research on the current efficiency of zinc deposition showed that apart from a low efficiency region at very low deposition rates ($i < 25 \text{ mA/cm}^2$), the efficiency up to the limiting current density is very close to 100% [21].

1.4 Dendritic Growth

A large body of work in the literature deals with the consequences of the dendritic growth of zinc deposits. As stated above, non-uniform deposits have undesired consequences in the operation of rechargeable batteries, as well as in electrowinning and refining. Striated deposits have ridges which are ohmically favored, and hence, lead to preferred growth. Eventually, the surface protrusions on the ridges of striations will begin to grow appreciably faster than the rest of the electrode, often resulting in dendritic, tree-like deposits.

A dendrite is a skeleton of a monocrystal [22]. It consists of a stalk and branches, resembling a tree. The angles between the stem and the branches or between different branches assume only certain definite and usually simple values in accordance with the space lattice. The main stem and the branches are formed from definite lattice directions. Quite often both the stem and the branches represent just one lattice direction, which is used to denote the dendrite variety [23]. That is, dendrites may be $[100]$, $[111]$, etc. Crystalline dendrites have an

increased surface free energy compared to the equilibrium shape of the crystal, and are therefore thermodynamically unstable.

Whiskers, in contrast to dendrites, have fast growth along an axis which is not a unique crystallographic plane. They are on the order of 1-50 microns in diameter, and up to a few centimeters long. They are distinct from dendrites in that they contain an axial screw dislocation, which determines the fast growth direction. Side faces are low energy planes which grow only slowly, or not at all [24]. For whiskers to emerge, the driving force for crystallization must be low to prevent two-dimensional nucleation and radial growth. Therefore, only under certain special conditions will whiskers occur, and then only in some metals.

Most metals when plated to sufficient thickness will evolve dendrites. Typically, soft metals such as Ag or Zn, which are also characterized by high exchange current densities, will evolve dendrites more readily than harder metals such as Fe, Co, or Ni [24, 25].

Experimentally, there seems to be an observed overpotential below which dendrites will not form. This may be as low as 2-3 mV in silver [24], and in alkaline zinc solutions it is in the range of 75-85 mV according to Diggle, Despic, and Bockris [26, 29]. The induction time before dendrites appear is a function of this overpotential. Low exchange current densities imply a larger critical overpotential for dendritic growth. Additives, either organic ones such as animal glues or metallic ones such as thallium, may lower the exchange current, and seem to inhibit dendritic growth. Any tentative models of initiation and growth must account for the fact that dendritic growth does not

always predominate. An analysis must be done to determine whether the growth interface is stable. Such an attempt was commenced by Mullins and Sekerka and later extended by Landau and Shyu [27, 28].

Mullins and Sekerka studied stability by introducing a perturbation in the original interface shape and determining whether it will grow or decay. Two effects were considered: a) a gradient effect (they considered only concentration gradients, but the theory can be extended to thermal or potential gradients as well), which promotes growth of the perturbation, and b) a surface-tension or capillarity effect, which promotes mass-transport from the tip to the base of the protrusion. The study was conducted under diffusion-controlled conditions, and the concentration field was assumed to obey Laplace's equation (i.e., both the surface and protrusion tip concentrations are much lower than the bulk concentration.) The perturbations were taken to be harmonic waves of wavelength λ on a spherical surface, since any surface profile can be decomposed by Fourier analysis into a series of such waves.

Mullins and Sekerka found that for radii greater than a critical value ($R_c = 7i^*$, where i^* is the nucleation radius given above as that of a stable nucleation site), the surface becomes unstable. Thus, for a 10% supersaturation, spheres larger than 0.14 microns are unstable [28].

At approximately the same time as the Mullins-Sekerka theory was being developed, Bockris and his co-workers at the University of Pennsylvania devised a series of propagation models for dendritic growth. In 1962, Barton and Bockris published the first comprehensive and quantitative theory of dendritic growth [29]. They assume diffusion-controlled growth with spherical diffusion at the dendrite

tip, but they neglected to include the effects of electric field. The predicted tip velocity did not agree with experimental results, probably due to the assumption of a hemispherical diffusion field. In addition, a hemispherical field generates an interface which changes with time. Consequently, the tip radius increases during the deposition process, according to the model, and contrary to observation. Diggle, Despic, and Bockris extended the model with mixed diffusion and activation control, but it still had the same shortcomings [24, 29].

Both models assume a maximum tip velocity, and paradoxically, a constant tip radius (which conflicts with the assumption of a hemispherical diffusion field). Therefore, the validity of their model extends only to the propagation stage of dendritic growth. This is shown schematically as the linear region in Figure 1.8. No attempt was made to account for the initiation of dendrites, or to explain their non-linear growth at short times.

Despic, Diggle, and Bockris [30] remedied this situation by proposing a model where the concentration at the tip of a small dendrite is a linear function of the ratio of its height to the thickness of the diffusion layer. The protrusion grows exponentially until it reaches a height equal to the diffusion layer thickness. At this point, the protrusion forms its own diffusion layer and the growth rate becomes constant. Extrapolating the linear region to zero dendritic height yields the so-called "induction time" (cf. Figure 1.8).

Barton and Bockris, and Despic's later theory assume that the tip current density is very small compared to i_0 , the exchange current density, which yields a linear kinetic expression. Along with a linear

concentration overpotential, they also assume spherical diffusion to the tip. They calculate an optimum tip radius by taking the derivative of their dendritic velocity expression and setting it to equal zero.

Diggle et al. [29], in a more elaborate version of the theory, which did not assume linear polarization, succeeded in explaining the frequency of dendrite formation in different systems. They gave a theoretical explanation for faster observed propagation rates in silver radii by reference to the calculated optimum radii. The calculated radius predicts faster growth in Ag than in Zn. Yet, such dendrites are less abundant than Zn dendrites because of the narrower range of optimum tip radii.

Even though the Bockris theories seem to provide quantitative explanations of propagation rates, several points remain unanswered. There is no explanation or modelling of interfacial instability or dendritic initiation, while field effects are completely ignored. Both the critical overpotential and initiation times lack theoretical explanation, and their prediction is also not possible. The effect of system parameters such as concentration, exchange current density, diffusion layer thickness, and the effect of additives are also not accounted for. Finally, the model gives no insight into dendrite shape and branching.

Landau and Shyu have recently applied instability theory to the study of dendritic growth, and have succeeded in refining the Despic, Diggle, and Bockris model of dendrite propagation [31]. They solved the instability problem by a series of steps. First, they solved the diffusion equation for the unperturbed interface. Then, an arbitrary infinitesimal perturbation (expressed as a series of harmonic functions) is

assumed, and by using the Mullins-Sekerka perturbation theory, an approximate solution for the case of the perturbed interface is obtained. The solution for the perturbed case is examined to determine whether the perturbations will grow or decay in time. If δ is defined as the amplitude of the protrusion, then $\dot{\delta}/\delta$ shows the ratio of the rate of growth of the perturbation to its amplitude. If the ratio is positive, the surface is unstable. The authors were able to derive a criterion for absolute stability as a function of the overpotential.

Stability analysis provides a relationship between the critical overpotential, below which no dendrites will grow, and the system's operating parameters. Plotting the critical overpotential versus current density reveals an extremely narrow stable region. A more careful evaluation of the model, however, reveals a much larger pseudo-stable region, where roughness growth rates may only be marginally larger than the flat surface growth rate.

To determine the position of this pseudo-stable region, a modified propagation model based on the work of Despic, et al. was employed. Instead of a circular tip, and the consequent hemispherical diffusion model, Landau and Shyu used a paraboloid of revolution as the geometry of their dendritic tip. This has the advantage of retaining its shape, and does not imply hemispherical diffusion. The new theory is in much better agreement with even Bockris' data, as long as a reasonable value for the zinc exchange current density is used. It should be noted that i_0 for zinc is not easy to determine because corrosion occurs simultaneously to externally driven deposition and dissolution.

Landau and Shyu's pseudo-stable region also explains the existence of induction times and a dendrite overpotential. The induction time may be characterized as the time necessary to evolve noticeable roughness, which may be conveniently taken to be ten microns. Referring back to Figure 1.8, it may be noticed that this induction time is different, and perhaps more accurate, than the one calculated by extrapolation from the linear growth region.

The induction time can also be determined from the exchange current density. This relationship clearly explains why Fe, Ni, and Co require high overpotentials and long deposition times in order for dendrites to appear. Any additive which affects the exchange current density will consequently affect the morphology of the deposit. Unfortunately, most organic additives break down after repeated cycling, and therefore their use is not advisable in rechargeable battery applications. The solution to uneven deposit morphology must come about, instead, from a better theoretical understanding of the hydrodynamics of flowing electrochemical cells.

1.5 Determination of Transport and Kinetic Parameters

The phenomena of striation emergence and dendrite initiation are a strong function of exchange current density (i_0) and local surface overpotential. Without adequate knowledge of the values of kinetic and transport parameters, no quantitative model of the morphology of zinc electrodeposits may be given.

Determining i_0 and the effective zinc diffusion coefficient are necessary before an analysis of the effects of recirculating flow may be

attempted. Anderson [16] proposed that recirculation lowers the local concentration overpotential by bringing fresh bulk solution to the surface, while the total overpotential remained fixed, leading to an increase in the local value of the surface overpotential. Such an analysis tries to explain how mass-transport could affect the deposit morphology well below the limiting current.

Fletcher [32], following Erdey-Gruz and Volmer [33], showed that the rate of three-dimensional nucleation is an exponential function of the square of the surface overpotential. Thus, even small changes in the surface overpotential may cause appreciable changes in the local current and nucleation rate, especially if the exchange current density is high.

To ascertain the value of i_0 , Jorne obtained Tafel plots of the zinc reaction [34,35]. His value of the exchange current density varied from one to five mA/cm² depending on the zinc concentration. Anderson obtained similar results, although his current-overpotential plots had a slight curvature downward, opposite of that expected as a result of cocurrent hydrogen evolution. Zinc corrosion may be one possible explanation for the curvature. Sierra-Alcazar and Harrison [36] did similar work on zinc-mercury amalgams, and found a linear relationship between i_0 and zinc ion concentration in dilute solutions. For concentrations above 0.1 M, their value for the exchange current density plateaued at 2 mA/cm², in agreement with Jorne and Anderson. Yamashita showed that this value could be changed simply by the bubbling of oxygen through the solution [37]. He reported a value of 50 μ A/cm² for i_0 , and postulated that the oxygen reacted with the zinc surface, leading to passivation.

The determination of effective diffusion coefficients has been less successful owing to the strong complexation of zinc with chlorine ions, when their concentration exceeds 1M. In our laboratory, Jaksic, with the help of Rajhenbah and Faltemier, attempted to measure limiting currents for zinc deposition on a rotating disc, and thereby determine the diffusion coefficient. They were only able to obtain results at very low concentrations, and even then their calculated diffusion coefficient varied with rotation speed. Cocurrent hydrogen evolution, which is not mass-transfer limited, probably acted as a constant background current during their experiments [38].

A complication in measurements of the effective diffusion coefficient is the tendency for zinc halides to self-complex at concentrations above 1 M, even forming negatively charged halo-zinc ions. Agnew and Petersen showed that the transference number of zinc becomes negative at concentrations above two moles per liter [39,40].

Therefore, diffusion coefficients measured by the capillarity method are much higher than values obtained electrochemically, since the latter values include a migration component [41]. Figure 1.9 compares the results of Hsie and Selman taken from polarographic measurements to those obtained by other methods [42-45]. Unfortunately, polarographic maxima due to nucleation processes on the mercury drop occur precisely when limiting currents are reached, thus complicating the determination of the correct diffusion limited current.

The best data available for binary coefficients are from the interferometric work of Rard and Miller [43], but their attempts to compute an effective diffusion coefficient in the presence of complexes was not

successful. Further, the effects of supporting electrolytes containing halide ions are still unclear. Figure 1.10 presents recent data by Selman et al. in concentrated bromide and chloride solutions [45]. No explanation for the observed minima in the diffusion coefficient is given. A consensus on the proper values for the diffusion coefficient in concentrated and well-supported electrolytes is still lacking.

Figure 1.1a. Zinc/chlorine battery [21].

Figure 1.1b. Zinc/bromine battery [21].

XBL 868-3205

Figure 1.2. 'CIFPLOT' of a micropatterned electrode.

a. Flow channel electrode

RE 5300, 45 MIN

b. Rotating disc electrode

400 RPM, 40 MIN

XBB 784-11239A

 1 M ZnCl_2 , PH 2.4, 30 MA/CM^2

Figure 1.3. Striated deposits.

- I – region of high enhancement
- II – region of attenuation
- III – region of moderate enhancement

Figure 1.4. Flow recirculation and mass transfer enhancement.

Figure 1.5. Development of striated deposits.

XBB 817-6215A

Figure 1.6. The dotted line is an Archimedes spiral described by, $\theta - \theta_0 = .0304 (r - r_0)$. The fine solid curve is a logarithmic spiral described by, $\theta - \theta_0 = 1.25 \ln r / r_0$. Note that the Archimedes spiral deviates greatly from the striation.

Effect of substrate on the appearance of the deposit

synthetic graphite
surface

(a)

platinum
surface

(b)

XBB 865-3607

$3\text{M ZnCl}_2 + 3\text{M KCl}$ pH=0.6 Re = 1000

23.9 mA/cm^2 $500 \text{ coulombs/cm}^2$ deposited

electrode dimensions 1 cm X 0.5 cm

Figure 1.7.

XBL 8611-9283

Figure 1.8. Dendrite induction time.

XBL 8611-9284

Figure 1.9. Effective diffusivities of zinc in chloride solutions.

XBL 8611-9282

Figure 1.10. Effect of supporting electrolyte on zinc effective diffusivities.

II. DESIGN AND FABRICATION OF THE MICROPATTERNED ELECTRODE

2.1 Overview

The design of an electrode with periodically spaced surface protrusions on the order of five microns in size required using both optical technology and microprocessing techniques in a clean room environment. The microfabrication facility in the Electronics Research Laboratory on the UC Berkeley campus has "class 100" clean rooms with less than one hundred particles one micron in size per cubic foot of air. Such an environment is necessary for most semiconductor fabrication procedures, and insures a contamination free surface. Figure 2.1 shows the scale of the desired surface features in relation to the single electrode size. Each electrode surface is a rectangle ten millimeters long, and five millimeters wide.

Since the processing requires several time-consuming steps, thirty-two electrodes were prepared in a single run, each with a characteristic set of patterns. The layout of the photolithographic mask used in the process is shown in Figure 2.2. The shaded areas denote regions of tighter dot spacing, which are enlarged in Figure 1.2 above. These patterns are arrays of dots or lines. The dots are placed in a square or triangular pitch pattern, while the lines are aligned either parallel or perpendicular to the leading edge of the electrode, which corresponds to the direction of flow in a channel flowcell. The use of microphotolithography allows precise definition of the pattern desired.

Figure 2.3 gives a schematic outline of the steps involved in the fabrication sequence. An optically-smooth surface is covered with photoresist and after prebaking, contacted with a chromium mask, then

exposed. After development and postbaking, the substrate is placed in a vacuum system, and gold is evaporated into the portions of the surface exposed during the preceding photolithographic step. The photoresist and overlying gold are then removed by liftoff; that is, dissolution of the resist in an appropriate solvent during ultrasonic agitation. An alternative is to pulse-plate the gold from a cyanide solution. After electrodeposition, the photoresist is removed by dipping the substrate in acetone, then rinsing in deionized water.

The electrodes are then separated by sawing along demarcation lines fifty microns in width. After applying insulating paint to the sides perpendicular to the patterned surface, the electrode is embedded in a teflon mount, and a wire is bonded to the backside. Epoxy is used to seal the substrate to the electrode holder.

A more detailed description of the process is given below. Substantial deviations from silicon processing techniques were necessary due to the unusual substrate materials employed. The required thickness of the evaporated material also presented problems, since 2.5 microns is an order of magnitude larger than the thickness of thin films in typical integrated-circuits.

2.2 Mask Generation

Creating a photolithographic mask using computer aided design software involves six steps, as illustrated in Figure 2.4. First, a graphical layout of the mask set must be made using "KIC", a public-domain design program [47,48]. KIC is an interactive, menu-driven graphics program for the laying out of integrated circuits. KIC employs

both symbolic layouts and has split-screen capabilities which, when used correctly, allow rapid location of desired features as well as fast compiling of design modifications.

The use of symbolic layouts, actually subcells called "instances", allows the design of complicated arrays by making the unit cell of the array the basic building block. Therefore, instead of mapping out the same circuit several times, it is sufficient to create a subfile with the correct dimensions, then refer to it by name and specify the location in the master cell where the instance should go. A box with the name of the subcell will appear on the screen, indicating where the subcell has been placed in the layout. This process may be repeated to obtain the desired circuit array. The advantage of this method lies in the greatly reduced amount of memory devoted to storing the master cell.

Saving memory space is a very important consideration. Booting up a complicated file (KIC allows the creation of 25 superimposable layers) requires up to an hour of real time. Furthermore, if allocated memory space is exceeded, a fatal error message is triggered, and the entire file is eliminated. Therefore, it is essential to always maintain a copy of the file in case of accidental memory overloads.

The split-screen capability allows one to use one of the screens as a magnifying glass to inspect and properly align small design features, while retaining a much larger field in the main window. Thus, one may inspect an instance, then move the cursor to another part of the layout without changing the display on the main screen. A four-button mouse allows commands to be entered by positioning the cursor and pointing with one of the buttons. Besides selecting a command or object,

pointing may define the center and size of the fine-positioning viewport or display the present position of the pointer in x and y coordinates [47]. Several Tektronix terminals are adaptable to the KIC program, though the 4107 is the most convenient, and allows the use of the mouse.

After the layout is complete, the file must be translated and flattened into a CIF (Caltech Intermediate Format) file using the "kictocif" program. Flattening is the process by which the sub-cells, or instances, are incorporated into the layout. The KIC file does not contain the information in the instance; rather, the KIC file only contains the name and position of the instance in the master cell. Translation is necessary for the file to be understood by the pattern generator that will create the mask. Also, a CIF file is necessary if a hardcopy plot is desired. To verify and troubleshoot the design, an actual hardcopy may be printed on a special plotter feeding paper three feet in width. Such magnification allows inspection of even the smallest details. Figures 1.2 and 2.2 are examples of such output reduced in size photographically.

The third step involves translation of the CIF file into a MANN file, a format understood by tape generating programs such as "m36gen." "m36gen" creates a tape with a digital coding of the pattern. This tape controls the generation of masks on a GCA MANN 3600 Pattern Generator. The pattern generator selectively exposes a mask by moving in discrete micron-sized steps and opening a two by two micron shutter, thereby allowing light to strike the chromium plate. The movement of the pattern generator is confined to "manhattan angles" (that is, only right angles are permitted, in analogy to New York City streets, Broadway

excepted). This limits the designer to the creation of square or rectangular holes. To obtain circular protrusions, selective underexposure is necessary in subsequent steps, as detailed below.

Chromium masks yield a dark field, creating a positive image of the original KIC layout. Emulsion masks, on the other hand, form a light-field or negative image of the designed pattern. For the present application, chromium masks have several distinct advantages.

Line delineation is much more precise using dark fields, and since the features cover only a small fraction of the entire mask (approximately 10% of the surface), the machine time for generating the mask is lower for the chrome process. This is in spite of the fact that generation of emulsion masks is generally faster for jobs of identical size. The machine requirements are not trivial, since our mask contains 129,500 features (a single line is made up of many such features strung together), and used twenty-one straight hours of machine time to expose. The pattern generator was also subject to aborted runs, and suffered relatively long downtimes. Adding in the time expended in aborted programs, fifty machine hours over the course of three months were needed to generate the complete mask.

The exposed plate, removed under yellow lighting, is then taken to a microprocessor controlled APT chrome mask developer. The mask is placed on a Teflon chuck in the enclosed vessel, and the development process is monitored through a clear plastic front panel. The mask is first spun at high speeds and rinsed with deionized (DI) water to evenly wet the surface. It is important that the photoresist side is up, and

that the mask is securely positioned. Otherwise, uneven development, or damage to the mask may occur.

After the rinse cycle, Shipley Microposit Developer in a 1:1 mixture with DI water is then applied continuously for thirty seconds through nozzles in the ceiling of the vessel. This is followed by a fifteen second rinse. A high intensity lamp is then lit and a concentrated chromium etchant is sprayed on for a minute. The etchant consists of Ceric Ammonium Nitrate $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$ and nitric acid in an aqueous solution. The etchant is a strong acid oxidizer with an orange color, and has severe toxicity if inhaled or swallowed. Therefore, the chamber in which the development takes place must be thoroughly rinsed after use.

After rinsing, concentrated developer is added to remove the remaining resist. A final cleaning step involves spraying acetone, followed by methanol, on the mask to remove any organic residue. The mask is then given a final rinse, and spun dry. Inspection of the mask is combined with optical microphotography. The resulting pattern of square holes is shown in Figure 2.5.

Since the mask generation process is rather involved, two copies of the mask were made on the Ultratech mask copier shown in Figure 2.6. The operator loads a blank mask on the door, and an exposed and developed mask on the face of the machine. Closing the door and setting the vacuum in operation triggers the automatic exposure of the blank mask. The time of exposure may be controlled to within a tenth of a second. A normal exposure lasts about a minute.

2.3 Surface Preparation

To fabricate ohmically favored protrusions on the scale of one to ten microns in height, it is necessary to prepare a surface which is of optically smooth quality. This degree of smoothness insures that the protrusions will be much larger than surface irregularities. The original idea envisioned a set of permanent electrodes which would be processed once, then used repeatedly. The materials chosen, for reasons detailed in Sec. 4.1, were platinum and gold. Platinum alloys more slowly with zinc than does gold, so initial studies focused on this material.

A piece of platinum metal, 2.54 mm (100 mils) thick, and measuring 5.08 cm (two inches) on a side, was polished in the Optics Lab at the Lawrence Berkeley Laboratory. The platinum was machined to size, then mechanically polished with successively finer grades of diamond paste and alumina. The final polishing was done by embedding the platinum in wax and using an optical lapping machine. The softness of the metal presented several difficulties, however. The emergence of "orange peel", a rippling of the metal surface, repeatedly occurred as the smoothness of the surface was improved. With the emergence of orange peel, the entire polishing procedure had to be started over. Chemical polishing with caustic solutions merely exacerbated the problem by pitting the platinum. After polishing, an optically smooth finish was obtained. The histogram of surface heights is given in Figure 2.7. The root-mean-square deviation from the mean is 30 Angstroms, while the peak to valley average height is 159 Angstroms, both of which are

insignificant in comparison with the height of the planned pattern. The surface may therefore be considered smooth before patterning.

Since gold is even more difficult to polish than platinum, an alternative surface preparation technique was employed. A piece of copper was first milled to the same size as the platinum substrate, and coarse-polished with successively finer grades of sandpaper up to 600 grit. Kerosene was used as a lubricant, requiring ultrasonic degreasing in organic solvents. The copper was taped to a polishing jig and fine-polished with 1.0 micron, 0.3 micron, and 0.05 micron alumina particles successively, in an aqueous paste using distilled water. The copper was then mirror-smooth, though several pitholes were observable at 200x magnification. The surface was then polished electrochemically, by dissolution in phosphoric acid at the limiting current. The surface became considerably shinier, and the number of pitholes decreased, as well as their size.

After thorough cleaning, the copper was placed in a Veeco 401 vacuum chamber, and a 1.00 micron layer of gold was evaporated on the surface. Adhesion was excellent since no native oxides exist on the surface, and gold alloys readily with copper. All processing steps were then done on the evaporated gold surface which maintained the optical property of the underlying copper, but displayed fewer pits. The polishing of copper was accomplished in less than a week without recourse to special optical methods. This allowed the researcher to create several substrates in a cost effective manner, allowing a broader examination of process alternatives.

As a result of platinum's near refractory melting point, evaporation became a large obstacle in the creation of the patterned surface. It is fortunate, therefore, that gold substrates could be prepared to replace the original platinum surfaces, without resorting to expensive and time-consuming polishing methods. Degradation of the processed surface became a less serious concern, since the low cost of the copper allowed for a much larger number of electrodes to be made.

After preparing a smooth surface, it was possible to begin the photolithographic steps in the fabrication procedure.

2.4 Photolithography

The photolithographic procedure begins with the spinning of a photosensitive polymer on the substrate. Application of photoresist is most successful if preceded by a thorough cleaning of the substrate in dilute sulfuric acid, then TCH, acetone, and methanol, followed by a final rinse in ultrapure water with a resistivity of greater than 17 megohms. The resistivity of the water is inversely related to the concentrations of ionic impurities in it. 18 megohm water contains less than 1 ppb total impurities, while 14 megohm water, with no more than 20 ppb of impurities, is discarded as being contaminated. Needless to say, an ungloved finger may contaminate over 10 liters of pure water.

Hexamethyldisilazane (HMDS) is widely used in the semiconductor industry as a treatment to improve photoresist adhesion, especially to oxides. The HMDS reacts with the oxide in a process known as silylation, forming a strong bond to the surface. At the same time, free bonds are left which readily react with the photoresist, enhancing photoresist

adhesion. Even metal surfaces, which may contain small amounts of surface oxides, benefit by HMDS pretreatment. The chemical is applied by placing the substrate in a saturated gas chamber filled with HMDS for one minute. The vapor condenses on the metal, forming a surface film. Since the accidental inhalation or absorption of HMDS has unknown toxicity, exposure should be minimized.

To spin the photoresist on the treated surface, the substrate is placed on a vacuum chuck. The controls were preset for both speed and time on the spinner. The standard recommendation for Shipley 1450 J is a speed of 5,500 rpm for 30 seconds to obtain a 1.0 micron thickness. A minimum speed setting of 2,000 rpm results in a 2.65 micron thickness as measured on the Alpha-step profilometer. AK 3770 photoresist was also used at 2000 rpm to obtain thicker films up to 6 microns in height. Both materials used are positive resists.

After placing the wafer on the chuck, one applies approximately 2 cm of photoresist in the center for a 5.08 cm (two inch) diameter wafer and activates the spinner. After it has automatically stopped, one shuts off the vacuum and removes the substrate. Before exposing, a pre-bake in a hot-plate oven at 90°C for thirty minutes is necessary to remove solvents from the photoresist.

The pattern generated on the chromium mask has features that are the actual size desired so that a contact printing method may be employed. Most optical reduction methods are designed with silicon wafers in mind, and do not accommodate a surface as thick as the one employed here. Kasper contact printers elevate the substrate until it touches the mask, which is held in place by a vacuum. The aligner used

is shown in Figure 2.8. The air gun in the photograph is used to dust off both the mask and the photoresist surface. Since the depth of field is slightly less than one micron, even a single dust particle may lead to an unevenly exposed surface. If the surface is not properly exposed, the photoresist may be only partially removed during development and the underlying substrate will not be reached.

The exposure time varies with thickness of photoresist. Overexposure leads to slightly larger features, while underexposure yields edges which are rounded. Exposure times used in our runs were 50 or 100 seconds, respectively, for the Shipley 1450 J and AK 3770 photoresists.

Development in a 1M KOH solution took approximately one minute. Appropriate developing times were determined by microscopic inspection under yellow-light illumination. Exposed holes in the photoresist are shown in Figure 2.9. After development, and a post-bake at 120° for 15 minutes, ordinary light will not affect the photoresist. The evaporation and pulse-plating steps are then performed.

2.5 Evaporation, Pulse-plating, and Liftoff

Physically deposited thin films and semi-conductor applications can either be sputtered, evaporated, or pulse-plated from electrolytic solutions. Sputtering rates are too low for films thicker than 0.1 microns in height. Therefore, for use in the fabrication of a micropatterned electrode, only evaporation and pulse-plating were considered. The evaporation system is shown in Figure 2.10.

Evaporation has the distinct advantage of being intrinsically free of contamination since it is done in vacuum. Both platinum and gold

were evaporated onto a patterned substrate. Figure 2.11 shows the vapor pressures and melting points of the respective metals. It may be noted that the melting point of platinum is close to that of the refractory metals, such as tungsten. Such refractory materials are used as the crucibles, or boats, in thermal evaporation.

All attempts to deposit platinum were limited by the formation of a platinum-tungsten eutectic melt, which dissolved the bottom of the boat and prevented further evaporation. The platinum that was successfully evaporated measured less than 1000 angstroms in height. Radiation from the glowing crucible overheated the masking polymer film, causing it to carbonize. Lift-off, the process of dissolving the film in an organic solvent, was therefore unsuccessful. Further attempts to create a platinum permanent microelectrode were abandoned in favor of the use of gold-coated copper.

Gold, as is apparent from Figure 2.11, has a much lower melting point which allowed for the evaporation of micron thick thin films. The underlying photoresist was not damaged during the evaporation. Adhesion, however, was poor due to the ductility of the evaporated gold. The thin film peeled off in a continuous layer and the portion within the defined pattern failed to bond to the underlying copper.

In an attempt to improve adherence, gold was evaporated onto the copper before patterning. Even so, subsequent evaporation of gold on gold also gave poorly adherent films, although the quality of the underlying film was excellent. It was then decided to use pulse-plating of gold to define the micropattern.

The Engelhard E-55 Acid Gold Plating Process [49] was employed to provide a high quality, 24K deposit. The solution is slightly acidic (pH 5-6), and uses a gold cyanide solution in conjunction with potassium cyanide and pH buffers. A temperature of 60°C and a current density of 10 mA/cm² was selected.

The electrodeposited metal was somewhat porous in nature, but when plated over an underlying evaporated gold film, it produced adequate patterning.

The resulting electrode will be used in future studies on the morphology of zinc electrodeposition. The ensuing chapters detail material selection criteria and preliminary experimental studies in a rotating disk system with smooth electrodes.

XBL 869-11682

Figure 2.1. Micropatterned electrode.

XBL 8611-4777

Figure 2.2. Lithographic mask layout.
 Actual electrodes are 5 mm x 10 mm. Dots are 5 microns in diameter, and lines are 5 microns in width. Dark areas of those of densest dot spacing.

XBL 869-11683

Figure 2.3. Process sequence.

Mask making flow chart

XBL 869-11681

Figure 2.4.

a. Triangular pitch

50 microns

XBB 868-6570A

b. Square pitch

Figure 2.5. Photograph of chromium mask.

CBB 868-6749

Figure 2.6. Ultratech mask copier.

Clean platinum surface before evaporation

Surface profile

Histogram of surface heights

XBL 869-11680

Figure 2.7.

CBB 868-6747

Figure 2.8. Kasper mask aligner.

XBB 868-6744A

Figure 2.9. Photoresist after development.

CBB 868-6751

Figure 2.10. Veeco evaporation system. The Belljar has been raised, and shutter (foreground) removed to view the tungsten boat. Electrodes at either side are clamped to the boat. The chimney is made of Pyrex.

XBL 8611-9281

Figure 2.11. Comparison of platinum and gold vapor pressures.

III. APPARATUS AND PROCEDURES

3.1 Experimental Apparatus

a) Electrolysis Cell

A three-compartment cell with an insertible Luggin capillary and a fritted-glass separator between the anode and cathode compartment was built to be used for rotating disk experiments. The acrylate lid had openings for the rotating disk as well as a nitrogen sparger and thermometer. Nitrogen, saturated with distilled water in a bubbler, was used to strip dissolved oxygen from the solution. The cell allowed accurate and reproducible placement of the Luggin capillary, and prevented anodic products from migrating to the cathode. Figure 3.1 shows components of the electrolysis cell.

All glassware was washed with soapy water, triple rinsed with distilled water, then soaked in HCl to leach out impurities. Finally, it was rinsed again with distilled water.

b) Electrodes

1) Anodes - Sacrificial zinc anodes were used during the stripping coulometry, and whenever substantial amounts of charge was passed. In the voltammetric experiments, a platinum foil counter electrode was used instead. The zinc used as an anode material was either 99.9999% zinc wire, or metallurgical grade zinc rods coated with insulating paint, except for an exposed face, and bonded to an insulated copper wire on the reverse side. As expected, the purity of the zinc gave no appreciable differences in our results owing to the borosilicate fritted-glass separator between the anode and cathode compartment.

2) Cathodes - The work involving the rotating disk utilized a large variety of electrodes, shown in Figure 3.2, which were fabricated in-house by previous researchers and by Pine Instruments:

a. Carbon Surfaces

- 1) Gould Synthetic Graphite
- 2) Pine Instruments Glassy Carbon
- 3) Pyrolytic Graphite
- 4) Union Carbide (HOPG) (Highly-Oriented Pyrolytic Graphite)
- 5) Exxon Graphite Loaded Polymer (used as a stationary electrode).

b. Platinum RDE

c. Gold RDE, manufactured by Pine

c) Instrumentation

All the voltammograms and most galvanostatic experiments were performed with PAR potentiostats Models 173 and 371. The 173 allows change from potentiostatic to galvanostatic operation by the flip of a switch, but is limited to one ampere maximum current. Limiting currents for concentrated solutions exceed this value, so the 371, which necessitates an external resistor for galvanostatic operation, was also used. A PAR Model 175 Universal Programmer controlled the potentiostat during cyclic voltammetry. Cell current was recorded using a PAR Model 379 Digital Coulometer. Figure 3.3 shows the actual experimental apparatus.

In July, 1986, a new PAR Model 273 was interfaced with a DEC LSI-11 digital computer. By programming the desired potential or galvanostatic steps, the experiment could be automated, with the data recorded and stored in digital form.

d) Electrolyte solutions

All solutions used in this study were prepared from analytical grade chemicals. All experiments were performed in acidified zinc chloride solutions supported with potassium chloride, except for coulometric studies in copper sulfate to determine the accuracy of the experimental method. The chemicals used were:

- (1) Mallinckrodt AR-grade Zinc Chloride
- (2) Mallinckrodt AR-grade Potassium Chloride
- (3) Mallinckrodt AR-grade Zinc Metal Dust
- (4) Baker Dilut-it Analytical Hydrochloric Acid
- (5) Mallinckrodt AR-grade Cupric Sulfate

3.2 Details of Operation

a) Electrolyte Preparation

Zinc chloride solutions were prepared in concentrations from 0.1M to 3M, with 1M KCl as the supporting electrolyte. The solutions were corrected to the desired initial pH by additions of hydrochloric acid. Zinc chloride evolves a substantial amount of heat when dissolved. This hastens the dissolution process, since the solubility is higher at elevated temperatures.

The zinc electrolytes were prepared in batches of four liters, then purified by cementation with zinc dust. The zinc replaces more noble metal impurities such as Fe, Cu, Mn, and Co. The dust is added to the solution (10 grams/ liter), then the solution is heated to 90°C while being stirred by a magnetic stirrer. The solution is kept at 90°C for 24 hours, then cooled and filtered. Residual cloudiness due to zincate ion formation is eliminated by addition of HCl or by refiltration.

The concentration of the zinc chloride solutions was determined independently by atomic absorption and by titration with EDTA, a chelating agent. The method employed for EDTA titrations is described by McVay [21].

Cupric Sulfate solutions were prepared with analytical grade reagents and used with no further treatment.

b) Electrode Polishing and Pretreatment

All substrates except the Exxon graphite loaded polymer were polished using 600 grit sandpaper, then 6 micron diamond paste, and finally 1 micron diamond paste. Samples were cleaned between each polishing step in an ultrasonic bath of Liqui-Nox detergent and distilled water; this ensured that the particles were not carried to successive polishing steps. After polishing, the electrodes were degreased, since the solvent used was kerosene. They were immersed in methyl ethyl ketone, acetone, and ethanol successively. All substrates were rinsed with distilled water and allowed to drain before immersion into the electrolyte.

Electrodes used in the microfabrication work were further polished as described in Chapter 2.

c) Experimental Procedure

Stripping Coulometry involved galvanostatic deposition of 0.1 to 20.0 coulombs per square centimeter on a rotating disk electrode rotated at speeds ranging from 200 to 1200 RPM. Deposition current densities of 10 to 1000 mA/cm² were maintained. After deposition, the deposits were stripped either galvanostatically at current densities of 50 and 100 mA/cm², or stripped potentiostatically at -0.5 vs. SCE. The PAR Model 173 Potentiostat-Galvanostat and Model 379 Digital Coulometer were used to set the current and monitor both the potential response, and charge passed. A PAR Model 175 Universal Programmer was used to generate triangular waveforms during cyclic voltammetry. Figure 3.4 illustrates the electronic configuration employed.

XBB 868-6845

Figure 3.1. Components of electrolytic cell.

XBB 868-6847

Figure 3.2. Rotating-disk cathodes.

XBB 868-6349

Figure 3.3. Experimental apparatus.

XBL 8611-9286

Figure 3.4. Equipment interconnections.

IV. RESULTS AND DISCUSSION

4.1 Selection of Reproducible Electrode Surfaces

Several electrode materials were evaluated for potential use in coulometric and flow cell experiments. Cyclic voltammetry was used to study their activity and to determine which electrochemical reactions occur during electrode pretreatment and subsequent zinc deposition.

For nucleation studies, a reproducible and essentially inert surface is desired, so that repeated cycling does not induce large changes in the electrode surface structure. There are two additional criteria that have to be met for use in the coulometric studies of zinc deposition: high hydrogen overpotential, and ideally polarizable behavior in the region anodic of zinc deposition. In coulometric stripping, the potential is stepped above the zinc potential, and the amount of zinc stripped is determined from the charge passed. Competing faradaic reactions, such as oxidation of the substrate or continued hydrogen evolution, contribute to the total current, and the actual amount of zinc on the surface can no longer be determined accurately.

Ideally, it was hoped that a single surface combining all these features would be found. Two categories of electrodes were studied: the noble metals platinum and gold, and carbon electrodes ranging from glassy carbon to pyrolytic graphite, including Exxon graphite loaded polymer.

4.1a Noble Metal Electrodes - Platinum and Gold

Noble metal electrodes generally differ from carbon, since they have lower hydrogen overpotentials and often display multiple adsorption

and underpotential peaks. A brief review of under-potential deposition is given in the Appendix. The materials tested were platinum and gold. Platinum electrodes have been used in the past as inert substrates for a variety of metal deposition studies. Only recently has work on the preparation of platinum surfaces given cause for concern over the chemical inertness of platinum electrodes.

Figure 4.1 shows the results of a "window-opening" experiment (successively widening the potential range used with each sweep) done on a polished and pretreated platinum electrode in a 1M ZnCl_2 solution at pH 5. This pretreatment, previously employed in this laboratory by Tsuda and Anderson, consisted of repeated cycling from slightly above the zinc potential to well into the oxygen evolution potential region. Hydrogen adsorption and oxide formation peaks were observed at potentials near the saturated calomel electrode (SCE) potential, as previously reported by Despic and others [50,51]. Peaks I' and II' have been identified by prior researchers as hydrogen desorption [51,52], and peak I is a corresponding adsorption peak. Hydrogen adsorption is quite reversible, but the peak associated with II' is obscured by the faradaic reaction labelled as II. Window-opening shows that peak II increases in magnitude as the anodic limiting potential is increased, thus allowing identification as platinum oxide reduction. The reduction is very irreversible, as demonstrated by the large potential separation of peaks II and III', the potential at which platinum oxide first forms.

Two types of platinum oxide are presumed to form. The shoulder labelled III' is the first to form, while the second occurs at higher potentials. Gilman prefers to treat the shoulder as chemisorbed oxygen,

since there is evidence that it forms a surface layer with a 1:1 ratio of platinum to oxygen [51]. Higher potentials yield larger ratios, thus making the oxide configuration more probable. This second variety of PtO_2 does not readily reduce itself, and turns a shiny metallic platinum surface into a dull gray. Its effect on hydrogen adsorption is dramatic. Figure 4.2 shows the same platinum surface before and after anodic polarization at 1.5 volts vs. SCE for 30 minutes in a ZnCl_2 solution supported with KCl. A fresh 1M ZnCl_2 solution purged with nitrogen at a controlled pH of 5 was used to measure both cyclic voltammograms shown. The hydrogen adsorption is markedly reduced and the peaks are broadened considerably, a sign that the surface has become less uniform. Repolishing is necessary to return the surface to its original activity.

Prior work on zinc deposition involved using platinum electrodes which had been anodically polarized before use. As a result of the present experiments, it appears likely that in such a case, deposition was carried out on PtO_2 rather than on platinum metal surfaces. Since the hydrogen evolution reaction, which on platinum involves H_{ads} , has been postulated by Epelboin as an intermediate step in the discharge of zinc [17], the extent of hydrogen adsorption may affect zinc nucleation behavior. Further, the existence of an oxide film which is not compact may mean that the real surface area is significantly larger than the geometric area would indicate [51]. In the present experiments, all platinum electrodes used were held below their oxidation potential at all times prior to zinc deposition.

Before the zinc deposition reaction occurs during a cathodic voltage scan, hydrogen evolution begins, and obscures the reversible zinc

potential. For our work, the cross-over potential during a slow quasi-equilibrium anodic potential sweep at 1 mV/sec, was taken to be equal to the equilibrium zinc potential. This value is about two millivolts negative of the tabulated value for the zinc reaction at unit activity, a result consistent with the formation of zinc complexes in the presence of a high concentration of chloride ions. A typical voltammogram on platinum is given in Figure 4.3. Higher cathodic currents during the backward anodic sweep are a direct result of nucleation occurring during the forward scan as shown by Fletcher et al. [32].

There has been controversy in the literature as to whether a zinc monolayer deposits on platinum below the zinc equilibrium potential. Despic and Pavlovic [50] claim that underpotential deposition occurs, as well as an alloying process. Their only supporting evidence is cyclic voltammetry. Despic claims that cathodic currents in excess of one mA/cm² were passed several hundred millivolts anodic of the zinc equilibrium potential, and attributes them to the process of alloying, completely neglecting the current associated with hydrogen evolution. Even the observed changes in slope may be explained without recourse to an alloying mechanism. It has been noted that impurities, especially iron, germanium, and cobalt, catalyze hydrogen evolution. When their deposition potential is reached, they plate out and accelerate the hydrogen reaction [53].

If alloying occurred, it would be possible also to see a corresponding anodic current due to the dissolution of the alloy. To examine this idea, a fresh platinum surface was prepared, stepped to the zinc equilibrium potential, and allowed to stand for over a minute. The

potential was then swept anodically, but no peaks corresponding to either UPD or alloy dissolution were observed. The sweep rate, originally 50 mV/sec, was increased to 100 mV/sec with no success. It therefore may be suggested that anomalous hydrogen currents are a direct result of catalyzing impurities.

The behavior of gold electrodes differs in that underpotential deposition of both zinc and copper may be observed. Copper UPD, from a dilute sulfate solution, is shown in Figure 4.4. Two distinct peaks are evident despite the fact that the gold electrode used was polycrystalline. In contrast, zinc UPD peaks are not as sharp as the copper peaks, because of the background hydrogen evolution, as seen in Figure 4.5. The peaks appear at the potential given by Kolb [54], but a second anodic peak appears closer to the zinc reversible potential. This second peak may be the anodic counterpart of Au-Zn alloy formation. Since zinc already exists on the surface in the form of a UPD layer, it would be difficult to assess whether alloy formation indeed occurs by surface detection methods. If the potential is held at this value, a steady-state cathodic current is obtained, corresponding to hydrogen evolution. Surprisingly, the UPD layer does not seem to inhibit hydrogen evolution very strongly. Chu, McBreen, and Adzic [55,56] also report zinc UPD and similar alloying behavior on gold.

In contrast to the results on platinum, no peaks corresponding to hydrogen adsorption are observed. This yields a region anodic to zinc UPD which is free of background current. The potential at which an oxide forms on gold is higher than on platinum, but when oxides were intentionally formed on the surface, they also resisted electrochemical

dissolution. Dipping the electrode in aqua regia, followed by mechanical polishing restored the original surface.

Stripping coulometry requires that the electrode used be free of competing faradaic reactions at the potential where measurements are made. Platinum fails to meet this criterion. Below the hydrogen adsorption potential, hydrogen evolution begins. Above this potential, oxidation processes occur. In contrast, gold meets the requirements, though not as well as the carbon surfaces discussed below.

For deposition studies, two factors offset each other. The existence of a UPD layer on gold and the possibility of alloying, which degrades the integrity of the zinc surface, limits the potential reusability of the gold electrode. Therefore, platinum will probably yield a more permanent surface. The trade-off is the existence of hydrogen adsorption, and its undetermined effect on the kinetics of zinc deposition. Nevertheless, difficulties in evaporating or sputtering platinum to the desired thickness led to the use of gold-plated copper, as detailed in chapter 2.

4.1b Carbon Surfaces

Commercial secondary zinc-halide batteries use carbon materials as substrates for zinc electrodes as an inexpensive alternative to platinum or gold. Carbon surfaces have high hydrogen overpotentials and are ideally polarizable over a wide potential range in acid media, as shown in Figure 4.6. The only significant cathodic process observed in a 1M ZnCl_2 solution is zinc deposition, which occurs at -1.09 Volts versus

SCE. Above -0.4 Volts, the background current is due to double-layer charging as the voltage is swept either cathodically or anodically.

Zinc deposition occurs at a slightly more negative potential than on platinum. The difference between the equilibrium zinc potential, and that at which significant current flows following the nucleation of three-dimensional growth centers, is called the nucleation overpotential. Extra energy is necessary to create zinc nuclei on foreign substrates, and the ensuing zinc deposit is a result of the growth and coalescence of such nuclei. An active surface would have many smaller nuclei at a given overpotential, while a less active surface would have fewer sites, which would force them to be larger in size after equal amounts of charge are passed. Concurrent hydrogen evolution occurs, with the hydrogen competing with zinc for surface sites. Since the overpotential of hydrogen on zinc is extremely high, a larger zinc surface coverage will yield a higher current efficiency.

Five carbon surfaces were tested for use in coulometric and flow-cell experiments: 1) Glassy Carbon, 2) Exxon Graphite-loaded Polymer, 3) Gould synthetic graphite, 4) pyrolytic graphite, and 5) Union Carbide Highly-Oriented pyrolytic graphite. The various surfaces are discussed below.

1) Glassy carbon is the name given to a range of amorphous or vitreous carbonized materials. It consists of condensed aromatic ribbon molecules which are oriented randomly and tangled in a complicated manner [57]. Their high resistance to graphitization suggests high stability, which supports the hypothesis that three-dimensional tetrahedral carbon structures exist in fully formed glassy carbon. Electron

micrographs show a layered structure, however. Kawamura reconciles this by proposing an interlocking structure, with each strand being multilayered. The absence of "loose ends," or unpaired carbon atoms at the surface, is the reason for its chemical inertness [57].

The results obtained by Anderson [16] on a glassy carbon electrode manufactured by Pine Inc. were duplicated in the present experiments. The surface is shown to vary in the density of zinc nuclei present in three separate regions on the same electrode surface. The first region shows very sparse nucleation, while the second and third regions demonstrate progressively denser deposits. The third region shows much denser nucleation, resulting in a "weblike" deposit after sufficient charge was passed. Figure 4.7 compares the two most disparate regions after deposition at fifty mA/cm² for nine seconds. It may be noticed that the crystallites in region 3 are larger, although less numerous. This non-uniformity would complicate the analysis of flow recirculation experiments.

The inhomogeneity and variable activity of glassy carbon surfaces has been studied by Kuwana et al. [58,59]. They found evidence for the presence of a thin carbon-particle layer on polished surfaces which dramatically affected the activity of the vitreous carbon electrode. Further, electrodes embedded in Teflon holders, such as the one used in these experiments, suffer from additional surface contamination due to teflon smearing over the electrode surface during mechanical polishing. The difficulty of preparing uniform glassy carbon surfaces made them unsuitable for use in either coulometric or flow-cell experiments.

2) The second material tested was Exxon graphite-loaded polymer. Its behavior was not adequate since the nucleation was very sparse. The surface contained dead spots which remained bare even after an average of two coulombs per square centimeter was passed during zinc deposition. Some hydrogen evolution was also noted.

The deposit was mossy even at low current densities, which is uncharacteristic for zinc plated out of acid solutions, though quite common in basic zincate solutions. Some polymer surfaces were coated with graphite felt, and were used as bromine electrodes in the Exxon battery. These surfaces, owing to their large surface area, gave very uniform deposits. The graphite felt does not hold up well upon cycling, however.

The Exxon materials were not considered farther because of their sparse nucleation and surface inhomogeneity.

3) Gould Inc. uses a synthetic graphite material as the zinc electrode in their commercial zinc-chloride batteries. Their graphitic material is made by pyrolyzing coke packed in a resin binder. The resulting surface has a very high nucleation density for zinc deposition, but the bare surface is very unhomogeneous as shown in Fig. 4.8. The "terrazzo-like" mosaic of carbon embedded in resins makes the surface difficult to characterize on the microscopic scale. It is surprising that an inhomogeneous surface such as this displays extremely uniform and high nucleation number density. The reason for this behavior is attributable to the penetration of zinc between carbon grains. Figure 4.9 shows the same electrode surface after repeated cycling above and below the zinc equilibrium potential. It appears that the carbon

particles themselves are broken up. Repolishing restores the original surface.

The reconstitution of the Gould electrodes explains aging effects observed during zinc deposition experiments. Deposits on a rotating disc, using a polished Gould surface, often suffer from non-adherence of the electroplated zinc. The deposit may either peel off or be torn off by the rotation of the disc. After several deposition and stripping cycles, however, the deposits adhere even after several hundred microns of zinc are plated.

Gould electrodes were used by McVay in current efficiency studies because of their high nucleation density [21]. McVay determined that the current efficiency of zinc deposition from concentrated solutions is uniformly above 95%, except at low current densities. Reports of bubbles emerging during discharge also appear in the literature [44]. Zinc deposition studies were performed in acidic conditions at low zinc concentrations to establish whether hydrogen evolution may accompany the dissolution of zinc. Compact zinc deposits were grown to an approximate thickness of 250 microns, then dissolved above the hydrogen evolution potential, but well below oxygen evolution (in a range from -200 mV to +400 mV vs. SCE, in 0.1 M ZnCl_2 and 1.0 M KCl at pH 1.3). On several occasions, bubbles appeared on the center of the electrode after complete zinc dissolution, but no gassing was observed before or after the dissolution process. It became apparent that these bubbles must have evolved on the electrode before the anodic stripping took place.

To test this hypothesis, a 200 micron-thick zinc deposit was removed from solution, and the zinc was peeled off carefully. In the

center of the resulting zinc disc, on the side facing the carbon electrode, there were numerous hemispherical indentations which ranged in size from 25 to 50 microns in diameter. They were clustered in the center of the disc, and did not occur on the edges. They seem to correspond to the site of hydrogen bubbles which attached themselves to the surface and were overgrown by the surrounding zinc deposit. Figure 4.10 shows an optical micrograph of the zinc surface, and the pits which cratered the zinc-carbon interface. The parallel lines observed follow sanding marks on the electrode surface.

Gould synthetic graphite was used for coulometric experiments in the early stages of the project, and for comparing results with those by McVay, but was later replaced by Union Carbide HOPG, which is discussed below. The restructuring of the surface after zinc deposition made it unsuitable as a substrate for a permanent micropatterned electrode.

4) Pyrolytic graphite differs from amorphous carbon and synthetic graphite because of its anisotropic structure. The basal plane is electrochemically inert, while the edge plane displays much higher activity. An electrode with exposed edge planes was not amenable to polishing. Figure 4.11 shows the structure of the pyrolytic graphite electrode after polishing with diamond paste. Although the surface is free of scratches, it is highly nonuniform, and is not flat. The waviness of the surface exceeds ten microns in height even after several different polishing methods were employed. Ordinary pyrolytic graphite was not used in this study due to the difficulty in preparing an acceptably smooth surface.

5) Union Carbide Highly Oriented Pyrolytic Graphite (HOPG) was the carbon material that showed the greatest surface homogeneity, and was used for the majority of the stripping coulometry experiments. When polished with diamond paste, the surface is shiny black with no visible scratches or pits. Even under 1000x magnification, no surface features are noticeable. The nucleation density was determined by Anderson to exceed that of all other carbon materials [16]. Its voltammetric response is flat between zinc deposition and oxygen evolution with no faradaic reactions readily apparent.

After continued use of the HOPG electrode, two phenomena were encountered which limited its usefulness, though they could be avoided by a judicious selection of experimental parameters. The first was a brittle failure of the electrode surface at the edge of the disc, where the carbon material abuts the epoxy holder. Figure 4.12 shows the fractured surface, exposing the individual graphite layers. Notice may be taken of the homogeneity of the intact surface, in comparison to the disordered nature of the failure zone. Figure 4.13 magnifies the lower portion of the previous figure, and shows zinc nuclei ensconced between successive carbon edges. Coarse grinding and subsequent polishing restore the original surface.

The second, and perhaps related phenomenon was the discovery of a "hard-to-strip" zinc deposit which remained on the surface even after polarization to potentials where oxygen began to evolve. This anomalous behavior occurred only after the electrode had been previously cycled into the oxygen evolution region during galvanostatic stripping of the bulk zinc deposit. Similar deposits on copper have been attributed to

the possible formation of zinc silicides by Ross [60] in alkaline solutions.

Figure 4.14 is a low magnification SEM photograph of the graphite electrode. Clusters of crystalline deposits may be seen on the surface. Figure 4.15 shows one such cluster, with each "grain" approximately ten microns in width. The localized nature of the deposit, identified as a zinc compound by EDAX x-ray detection, makes its compositional analysis difficult. After rinsing the electrode in nitric acid, the deposit disappeared. Several alternative explanations were investigated, including the intercalation of zinc chloride into the HOPG material, surface oxidation of the carbon electrode, and the existence of impurities in the electrolyte solution.

Intercalation involves the penetration of the graphite material by either anions or cations, resulting in an increase in the lattice parameter, and a corresponding increase in the conductivity of the electrode. It would explain the failure of the electrode at the edges, since the increase in the lattice size would create a stress at the carbon-epoxy boundary. Metal chloride-graphite intercalation compounds have been achieved by a thermal process at elevated temperatures [61], in the forms of manganese chloride, rhenium chloride, and cobalt chloride. The formation of graphite intercalation compounds (GIC) is an electrochemical reaction, however. The redox equivalents may be provided directly at an electrode [62]. Beck gives the overall reaction for a GIC of the acceptor type as:

where x = "degree of polymerization"

y = stoichiometric number for anions A^- reacting per C-atom

v = stoichiometric number for solvate acid molecules HA per anion.

HA = undissociated acid molecules.

This process requires a high concentration of undissociated acid molecules, which is lacking in the present (pH 3-5) solutions. Hence, the rate at which intercalation occurs would be extremely low. Further, the increase in conductivity does not coincide with the observed passivation phenomena. Therefore, fracture at the edge of the crystal is unlikely to be caused by electrochemical intercalation of chloride ions.

A related phenomena is surface oxidation of carbon materials, and the formation of intercalated "graphite oxide" [63,64]. The corrosion of graphite occurs at approximately +0.7 versus SCE, and results in both the formation of quinone groups on the carbon surface, and the evolution of CO_2 , which forms CO_3^{2-} in solution. While the voltammogram of HOPG graphite appears flat at intermediate scan rates, a rate of 50 mV/SEC shows a shoulder in the region normally identified with the oxidation of graphite [65]. This is shown in Figure 4.16.

The anodic destruction of graphite in aqueous solution, especially those containing chloride ions, "has been universally attributed to the oxidation of its surface by adsorbed atomic oxygen before the latter recombines into an oxygen molecule", according to Randin [64]. "Swelling occurs in the graphite, causing it to exfoliate." The simultaneous discharge of chloride ions also plays a role [64].

The existence of an oxide film would therefore explain the brittle failure attendant with polarization to anodic potentials, but does not account for the localized nature of the "hard-to-strip" zinc. If oxidation causes the passivation of the surface, a more uniform passive zinc layer would be expected.

The localized nature of the passive zinc deposit may be explained by analogy with the behavior of zinc corroding in hard bicarbonate water. According to Pourbaix, "a protective coating... made up of a mixture of zinc oxide and zinc carbonate, is formed when there is an intensive relative movement between zinc and aerated distilled water", especially in the presence of a high concentration of carbonate ions [66]. Figure 4.17 depicts the broadened passivation region in solutions containing CO_2 , as a function of pH. Near-neutral solutions are expected to form a passive film. At lower pH's this film is thermodynamically unstable and may be expected to corrode over time. The formation of zinc carbonate-zinc oxide crystals at the surface during the corrosion of graphite and vigorous oxygen evolution is the most likely explanation for the localized passive zinc deposits.

Copper carbonate and copper oxide films would be expected to behave similarly at even lower pH's. Passive copper was observed at pH 3 in a 0.1 M CuSO_4 solution following oxygen evolution on the same HOPG surface, corroborating the present hypothesis.

The consequence of the degradation of the graphite surface, and the accompanying formation of passive zinc and copper, prevented the use of galvanostatic stripping in coulometric experiments, since this involves a transient potential jump into oxygen evolution following the stripping

at the zinc deposit. Instead, potentiostatic stripping below the oxidation potential of graphite was used. The electrode remained free of damage, and "hard-to-strip" zinc was not observed during potentiostatic stripping.

4.2 Stripping Coulometry

Stripping coulometry allows the experimenter to measure current efficiencies for metal deposition reactions, since the hydrogen evolved on a rotating disk is forced away from the surface by convection and, therefore, the back reaction of hydrogen is negligible in comparison to the charge accompanying the dissolution of the electrodeposited metal. To obtain consistent results, a fixed amount of charge (from 1-10 Coulombs depending on the current range) was passed under galvanostatic conditions below the oxygen evolution potential. The resulting current efficiency was plotted as a function of total current. Alternatively, the zinc current (i.e., the efficiency multiplied by the total current) was plotted versus the total current to obtain limiting current plateaus.

When the limiting current is reached, two processes occur. First, the amount of charge going to hydrogen evolution increases in direct proportion to the increase in total current. Further, the morphology of the zinc deposit changes abruptly, from an adherent, though nodular deposit, to a powdery deposit which detaches itself from the electrode [67]. At this point, the measured zinc current efficiency falls precipitously, as shown in Figure 4.18.

Stripping Coulometry was used to obtain zinc limiting currents for use in calculating effective diffusion coefficients at a range of zinc and chloride ion concentrations. Two alternative methods were explored: potentiostatic stripping at a known potential where the background current was negligible (below 0.1 mA/cm^2), and galvanostatic stripping which allowed precise control of the rate of zinc dissolution. Figure 4.19 shows a typical result from the galvanostatic stripping experiments. A sigmoidal curve is obtained, as the potential does not abruptly change value when the zinc concentration at the surface goes to zero. Rather, a graduated transition occurs as a mixed zinc dissolution/oxygen evolution potential is measured. On HOPG graphite, as detailed above, this is accompanied by the formation of passive zinc carbonate or copper carbonate species forming on the electrode surface, leading to erroneous measures of zinc and copper deposition rates. On gold, gold oxide formation occurred, necessitating repolishing.

To circumvent these difficulties, potentiostatic stripping was used in all later experiments, and the results shown below represent those obtained by the latter method.

Stripping currents were $50\text{--}100 \text{ mA/cm}^2$, resulting in a ratio of $500\text{--}1000$ greater than the maximum background current of 0.1 mA/cm^2 . The charging current (totalling 6.0×10^{-5} Coulombs) due to stepping the potential between zinc deposition and potentiostatic stripping was several orders of magnitude smaller than the current due to dissolution, and hence ignored.

Figure 4.20 shows results from a dilute solution (0.1 M Cu SO_4). The diagonal line corresponds to 100% current efficiency. Copper

deposition only deviates from this as the limiting current is approached and the hydrogen potential exceeded. A fairly flat limiting current plateau is obtained, and a limiting current of 76.3 mA/cm^2 determined for a rotation rate of 800 RPM. This result was compared to the value predicted by Selman's correlation for copper limiting currents on a rotating disk, and found to agree to within 5 percent [67]. His correlation predicts a copper transference number of 0.031 and a limiting current of 73.3 mA/cm^2 . The error in the present experiment is attributed to the existence of surface roughness, which increased the actual surface area of the electrode.

The results for 0.1M zinc chloride were not as promising. Instead of a flat plateau, a slight slope still occurred before powdery deposits set in above 225 mA/cm^3 , as seen in Figure 4.21. The diffusion coefficient calculated from the Levich Equation [4] was $1.2 \pm 0.1 \times 10^{-5} \text{ cm}^2/\text{sec}$, approximately twenty percent higher than values reported in the literature [38,43].

At higher zinc concentrations, no plateaus were obtained. The zinc current efficiency remained close to 100% up to the maximum current of 1 Amp. At low current densities, the efficiency is much lower, as observed previously by McVay [21]. This was attributed to a competition between hydrogen and zinc for sites on the graphite surface. The increased nucleation number density accompanying higher current densities, leads to higher zinc surface coverage, and correspondingly higher current efficiencies. This is because of zinc's high hydrogen overvoltage. The relation between current efficiency and applied current is shown in Figure 4.22.

Stripping Coulometry failed to give the expected limiting current behavior. The slope in limiting current plots obtained by cyclic voltammetry [38] cannot be due simply to concurrent hydrogen evolution. Rather, surface roughness at higher current densities enhances the convective flow at the surface of the rotating disk, and increases the actual electrode area significantly. Thus, the Levich Equation no longer describes the diffusional process to the roughened disk, and the zinc current exceeds the predicted limiting value.

ZnCl₂ unsupported at pH 5.2; Pt electrodes; SCE reference

XBL 869-11684

Figure 4.1.

XBL 8611-9280

Figure 4.2.

XBL 869-11686

Figure 4.3.

XBL 869-11687

Figure 4.4.

XBL 869-11685

Figure 4.5.

Figure 4.6.

XBL 869-11689

a. Region 1 (Dense Nucleation)

b. Region 3 (Sparse Nucleation)

Figure 4.7. Glassy carbon substrate 50 mA/cm^2 , 9 seconds [16].

XBB 868-6743

Figure 4.8. Clean Gould surface before deposition.

XBB 868-6741

Figure 4.9. Gould Surface after dissolution of zinc deposit.

XBB 868-6742

Figure 4.10. Trapped hydrogen bubbles.
Lines correspond to polishing marks.

XBB 868-6263

Figure 4.11. Pyrolytic graphite (c-plane).

Figure 4.12. Brittle failure at edge of HOPG electrode.

XBP 868-6736

Figure 4.17. Brittle Failure of Ti/Pt electrode.
(Detail of Fig. 4.12).

Figure 4.14. HOPG surface after galvanostatic zinc dissolution.

Figure 4.15. "Hard-to-strip" zinc.

XBL 869-11688

Figure 4.16. Oxidation of HOPG electrode.

XBL 8611-9285

Figure 4.17. Zinc Pourbaix diagram.

a) without carbonate ion in solution.

b) with unit activity of carbonate ion.

Note: passivation region is greatly expanded.

Figure 4.18.

XBL 869-11690

Figure 4.19.

Figure 4.20.

XBL 8611-9275

Figure 4.21.

XBL 8611-9277

105

Figure 4.22.

XBL 8611-9278

V. SUMMARY AND CONCLUSIONS

Gold, platinum, and a number of synthetic carbon electrode surfaces were tested as suitable substrates for the fabrication of a permanent micropatterned electrode, and for use in coulometric experiments to evaluate limiting currents.

To obtain a limiting current for zinc deposition free from substrate effects, an electrode with high hydrogen overpotential and a high nucleation rate for zinc is desired. Union Carbide HOPG graphite displayed the most ideally polarizable behavior below 0.7 V versus SCE. Above the zinc equilibrium potential and below its oxidation potential, HOPG electrodes displayed a background current of less than one 50 microamps per square centimeter. Of the materials tested, Union Carbide HOPG graphite had the most favorable properties, and hence, was selected for use in stripping coulometry. Reproducible results were obtained, though at high current densities, roughness development obscured limiting currents.

In comparison, platinum displayed a number of hydrogen adsorption peaks, low hydrogen overpotential, and a reactivity which varied as a function of electrochemical pretreatment. Gold electrodes form a UPD layer with zinc, and still had a lower hydrogen overpotential than pyrolytic graphite. Other carbon materials, such as Gould synthetic carbon and amorphous (glassy) carbon displayed polarizable behavior, but failed to meet additional criteria. Glassy carbon was inhomogeneous on the macroscopic scale, with regions of varying zinc nucleation number density. Gould graphite is inhomogeneous, because it is composed of a car-

bon material in a resin binder. Repeated cycling into the zinc deposition region showed an aging effect, leading to a high nucleation rate and fewer non-adherent deposits.

After galvanostatic stripping on HOPG graphite, localized passive zinc crystals were observed, and identified as a zinc carbonate-zinc oxide mixture. The anodic dissolution of graphite, with oxygen coevolution, resulted in a high carbonate concentration. In the presence of zinc, this formed zinc carbonate. The passivated crystals were predicted to form in copper solutions as well; their existence was also observed. The graphite electrode demonstrated brittle failure at the carbon-epoxy interface, as a result of stress induced by the formation of surface oxides and possible intercalated "graphite oxide."

For use as a substrate in the fabrication of micropatterned electrodes, additional criteria had to be met. The use of microphotolithography coupled with evaporation and pulse plating to define micron-sized surface features requires a material that is able to form continuous thin films. Gold proved to be best suited for use, due to its low melting point and uniform deposition from cyanide baths. Copper was selected as the substrate because of its relative ease of polishing, low material cost, and good adherence to gold films through the formation of a surface alloy.

A micropatterned gold electrode with surface features five microns in diameter was designed and fabricated for use in future studies of zinc electrodeposition. It is envisioned that use of this electrode will help to elucidate the complex role of zinc growth centers in the development of striated deposits.

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To my father, less academic in outlook, but surely as wise, I extend a thanks for always encouraging me to disregard the pessimists, and to pursue instead the road seldom taken. I would also like to assure him that I have not lost my interest in economics, merely because I pursued electrochemistry instead. All Sutijas, so I am told, have seven concurrent careers.

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VIII. APPENDIX: UNDERPOTENTIAL DEPOSITION ON PLATINUM

A.1 Introduction

The term "underpotential deposition," or "UPD," describes the formation of a metal monolayer at potentials positive to the reversible electrode potential, where bulk deposition cannot occur. Understanding UPD is important when one is studying galvanic processes, since in metal deposition, such an electrosorption process often occurs prior to bulk reaction. Previously, the formation of nucleation sites was believed to be the first step in metal deposition [54]. Such nucleation is expected to occur on top of the UPD monolayer. Therefore, the effect of the substrate on the resulting deposit is largely determined by the properties of the UPD layer.

In 1912, Hevesy reported a deviation from Nernst's Law using radioactive metals deposited on a copper substrate. He plotted coverage-potential isotherms, and saw an asymmetrical tailing off for potentials more positive than the equilibrium value. This indicated that metal adsorption occurred at up to several tenths of a volt more positive potential than the reversible value [69]. Herzfeld, in 1913, explained this deviation from Nernst's Law by assuming that the activity of the solid varies with surface coverage θ . Herzfeld felt that the dissolution rate varied with surface coverage, while the rate of deposition of the metal ion in solution did not. This yielded a coverage-dependent equilibrium potential. Herzfeld's formalistic, perhaps ad hoc, explanation deterred further study of the phenomena until the late 1940's. At that time, Rogers and Stenhey used stripping analysis to study UPD. Thus, they deposited differing amounts of metal and measured the

potential of dissolution. They were able to decide between bulk and trace behavior and analyzed solutions with concentrations as low as 10^{-8} M. They extended the Herzfeld model and proposed that the reduction potential $E(r)$, is a function of surface activity a_{ML} , and an additional term, $E(a)$, which is a correction to the Nernst potential $[E(0)]$ which accounts for interactions such as alloying between the reduced species and the electrode substrate [61]. Their expression was:

$$E(r) = E(0) + E(a) + \frac{RT}{zF} \ln \frac{C(ox)}{a_{ML}} \quad (1)$$

where
$$a_{ML} = \begin{cases} \theta & \text{for } 0 < \theta < 1 \\ 1 & \text{for } \theta = 1 \end{cases}$$

$C(ox)$ = activity of the metal ion.

These early results were perhaps limited in scope, but clearly showed that monolayer deposition at underpotentials results from a strong interaction between the monolayer and the substrate, which may be modelled empirically as an activity less than unity for the deposit.

Lorenz used a twin electrode thin-layer (TTL) cell to study UPD [68], where the working and generator electrodes are 50 microns apart and have independent potential regulation. The reference and counter electrodes are held in a separate reservoir with supporting electrolyte. The generator electrode is composed of the same metal as that deposited at the working electrode, and represents a reversible metal/metal ion electrode. The working electrode is of a foreign metal on which UPD studies will be conducted. At an appropriate potential, the metal is deposited onto the working electrode, causing a current I to flow due to the reaction:

Integration of the current I at the working electrode yields the surface charge corresponding to the deposition process plus any non-faradaic currents such as double-layer charging, which is discussed below. Since the constant reversible potential $E(0)$ at the generator electrode will maintain a constant chemical potential for the metal ion, any change in the metal concentration due to deposition onto the working electrode will immediately be compensated by a respective current $I(g)$ at the generator electrode [54]. Consequently, if the adsorbed metal is uncharged, the cyclic voltammograms should be identical in shape and opposite in sign, save for the background non-faradaic current. In Figure A1, cyclic current-potential curves for Pb adsorption on Au are given. It can be seen by inspection, that to the first approximation, the magnitude and shape of I is identical to $I(g)$.

The background current, measured using a blank electrolyte, is shown as $I(b)$ in Figure A1. A blank electrolyte is one which does not contain the adsorbing metal cations, but preferably contains the same anions. In the TTL configuration, this may be attained by simply holding the potential of the generator electrode at a potential where the concentration of metal ions in solution is less than 10^{-9}M [69].

The compensation made by estimating the double-layer charging current using a blank electrolyte makes the assumption that the capacitance of the double layer does not change when a monolayer of foreign metal is deposited on the bare surface. Since the capacitance is proportional to the surface area, any roughening will necessarily result in a proportional increase in the charging current. It is fortunate that

these charging currents are generally small, often one may assume that the substrate electrode is ideally polarizable in the underpotential region [69,70].

In systems where other faradaic or sorption processes may occur, (e.g. coverage of the electrode surface by hydrogen or oxygen, anion adsorption, or the formation of alloys) special care must be taken to separate the processes. The formation of alloys is generally limited by low solid diffusion coefficients ($D < 10^{-16}$ cm/s) [69], while anion effects may be mitigated by non-adsorbing anions. The case of oxygen coadsorption is by far the most difficult problem to solve, though work by Chierchie tries to account for its effect on measured current [71].

Some authors later tried to model UPD by correlating the difference in potential between the first peak in the UPD region and the reversible Nernst potential to system parameters such as the electronegativity of the depositing ion.

A.2 The KPG Model

In 1974, Kolb, Przanski, and Gerischer (KPG) published a voltammetric study of 22 couples where UPD occurred [72]. Several had already been reported in the literature, but the results were complicated by the presence of an adsorbing cation, Cl^- . Using a TTL cell, KPG kept the metal ion concentration constant at 2×10^{-4} M, and ran cyclic voltammograms on their system. They found two anodic stripping peaks, one which corresponded to dissolution of the bulk phase (they had cycled to potentials slightly below the reversible potential), and one which they took to be characteristic of the UPD monolayer. $\Delta U(p)$ is the difference

between the two anodic stripping peaks. The underpotential shift $\Delta U(p)$ can be understood as the difference in the bond energies between the metal adatom on a foreign substrate and on the metal itself [70].

To establish a model which quantitatively explains why monolayer adsorption is energetically favored in comparison to bulk deposition, they correlated $\Delta U(p)$ versus other system parameters. Since in several systems, as noted above, partially discharged adatoms formed the monolayer, they felt that electrostatic interactions must play an important role in the phenomena [72].

Other workers had already correlated adsorption parameters with electronegativity. Therefore, it was generally accepted that the charge passed from the adatom to the metal was proportional to the difference in electronegativities of both [70]. The resultant chemical bond is slightly polar. Furthermore, Trassati and others had already shown that Pauling's electronegativity, $X(p)$, of an atom is linearly related to the work function, ϕ , of the solid by

$$X(p) = 0.5 \phi - \text{constant} .$$

Since the work functions of metals had been determined much more accurately than their electronegativities, KPG plotted $\Delta U(p)$ versus $\Delta\phi$. They expected that the ionic character of the metal-adatom bonding should increase with a corresponding increase in $\Delta\phi$, and that the ionic contribution to the chemical bond of the metal-adatom complex, arising from the partial charge transfer, was responsible for the deposition of the underpotential layer [72].

Figure A2 shows their plot, which has amazingly little scatter given the error in each of the measurements. They were even able to predict the underpotential at which lithium would adsorb on several foreign metals, even though they were the difference in work function was extrapolated by a factor of two.

Although KPG's results were impressive, they still failed to explain certain other characteristics of UPD. Usually, the monolayer adsorption on polycrystalline surfaces occurs around a single potential value, yielding one pronounced current peak in cyclic voltammetry. When single-crystal studies became more common, a discrepancy arose, since on polycrystalline surfaces the peaks were much broader than on single crystals. Often, there was a positive deviation from a Langmuirian isotherm in the polycrystalline case, and a negative deviation on single crystals. Furthermore, several systems displayed multiple UPD peaks, but no competing sorption processes occurred. It seemed that UPD was more complicated than anticipated, and that the KPG model would have to be modified to account for metal-adatom interactions.

The existence of a multi-peak UPD structure indicates a stepwise formation or dissolution of the adsorbed monolayer. In the case of lead deposition on gold, Yeager et al. [70] demonstrated that the substrate surface structure had a pronounced influence on the position and width of the UPD peaks. A controversy then arose about the interpretation of UPD in certain systems, such as Pb^+ on Au, where there were only small differences in work function between the substrate and the metal ion. The strong dependence of the work function ϕ on the crystallographic orientation was not completely reflected in the observed changes in

$\Delta U(p)$. The KPG model was unable to correlate the new data from single-crystal studies. Clearly, the adsorption energy of UPD is not only determined by the electronegativity difference of the bulk materials, as expressed by $\Delta\phi$, but is also strongly influenced by normal and lateral interactions depending on both the substrate and the adsorbate structure [73].

According to one view [71], the UPD peaks represent two-dimensional nucleation leading to phase formation in the metal monolayer deposition. The other view, held by Lorenz, is that UPD is an adsorption process that includes a strong interaction between adsorbed adatoms. The exceptionally narrow peak for UPD of lead on gold led Adzic [70] to assume a phase transition as its explanation. Lorenz countered that similarly sharp peaks in lead UPD on single-crystal silver, could be explained by the formation of an ordered structure among the adsorbed metal atoms [74].

Principally, two limiting cases of superlattice structure formation must be considered. The first is where the radius of the adsorbed atom is larger than the radius of the substrate species; the second case being where the radius of the adatom is equal to or smaller than the radius of the substrate metal. The second case, corresponding to 1/1 adsorption, allows the formation of epitaxial superlattice structures. In the former case of 1/n or "multisite" adsorption, the blocking of n adsorption sites leads to more complex ordered structures of different density and symmetry. It is principally due to this phenomenon that UPD surfaces alter the catalytic properties of the underlying material.

A (2×2) superlattice refers to the distance in crystal bond lengths that separate two adsorbed metal atoms. In this case, for every lattice position occupied by an adatom, a nearest neighbor position remains vacant though partially blocked. In the case of a hexagonal (111) lattice, the experimental coverage values are best explained by assuming one and two layers of filled honeycombs, for Pb and Tl adsorption respectively [75].

Besides the formation of superlattices, long-time polarization of the surface at UPD potentials leads to surface reconstruction phenomena, presumably due to the internal strain within the metal-superlattice structures. This effect was observed especially for Pb and Tl adsorption on (111) silver faces and gold single crystal substrates and was found not to be caused by specifically adsorbed anions.

Figure A1. Cyclic current-potential curves for Pb on Au, obtained in 0.5M NaClO₄ (pH 4.7 acetate-buffered) with a thin layer cell. Scan rate, 1 mVs⁻¹. $E_g = -0.565 \text{ V}_{\text{SCE}}$ $\triangle$ $1.8 \times 10^{-4} \text{ M Pb}^{2+}$. I, indicator current; I_g , generator current; I_b , base current (for $c_{\text{Pb}^{2+}} = 0$)

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Figure A2. 'KPG' model of underpotential deposition.

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UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720